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The Fluorination of Copper

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ABSTRACT

The reaction between fluorine gas and copper metal has been studied at 450°C and pressures from 10 to 130 mm Hg. The reaction was pressure dependent and followed the logarithmic law, $y = K \log (at + c) + C$. The logarithmic rate constant K varied with pressure according to the equation $\log K = m \log P - 6.11439$ where m is equal to 0.781. Analysis of the corrosion film yielded a F/Cu ratio of 1.11. A reaction mechanism is postulated, and from evidence presented fluorine is considered the migrating species in the reaction.

In the study of gas-solid reactions the variables to consider from a kinetic point of view are the effects that time, temperature, and pressure have on the rate of reaction. These variables have been studied in detail for the reactions of metals with oxygen, and many mechanisms have been postulated to account for the data; however, very little kinetic work has been attempted with the more reactive fluorine. The reaction of copper foil and fluorine gas has been studied at a pressure of 200 mm Hg and over the temperature range of 427°-649°C. The simple power law $y^n = kt$ was applicable at 427° and 482°C where n was 1.15 and 1.62 and k was 1.7×10^{-3} and 1.6×10^{-2}, respectively (1). A further increase in the temperature resulted not only in an increase in the rate of reaction but also in a change of rate law. In the temperature range 538°-649°C the logarithmic law $y = k' \log (\sqrt{t} + k'')$ was obeyed where k' varied from 1.2 to 1.5, and k'' was equal to 5.

Other studies of metal-gas reactions have reported both pressure dependent and pressure independent relationships. Hale et al. (2) found that the nickel-fluorine reaction was pressure dependent at high temperatures (594°-815°C) and pressures from 76 to 760 mm Hg. Brown, Crabtree, and Duncan (3) working at lower temperatures (100°-250°C) and pressures (6-60 mm Hg) found no pressure effect for the reaction between copper powder and fluorine. Jarry (4) using radiotracer techniques to study the mechanism of nickel fluorination has reported that fluorine is the migrating species in the nickel-fluorine reaction.

The object of this investigation was to study the effect of pressure on the reaction of copper and fluorine at 450°C and subatmospheric pressures and to set up a preliminary model of the mechanism.

Apparatus

Figure 1 is a schematic diagram of the apparatus used for the experiments. The entire system was Pyrex glass except for the pressure pickup and the connection between the system and the bottle of high-purity fluorine (99.8%) which consisted of copper tubing and a Teflon-packed Swagelok fitting. The cold trap, containing methyl cyclohexane slush (−116°C), was used to remove any hydrogen fluoride contaminant in the fluorine gas. The fluorine
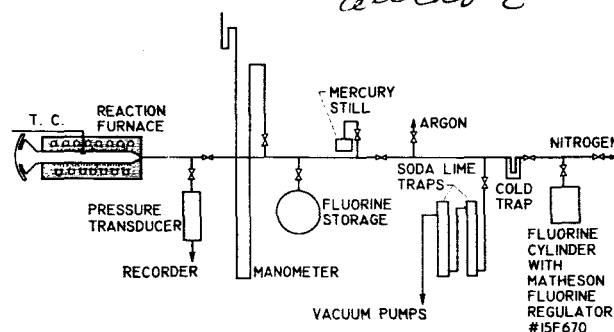

Fig. 1. Apparatus used for study of copper-fluorine reactions

was assayed by the mercury-reflux method (5). The mercury manometer used to measure the pressure in the storage bulb had a protective layer of fluorocarbon oil floated on top of the mercury to prevent the reaction of mercury and fluorine. All stopcocks and ground-glass joints were lubricated with fluorocarbon grease.

The quartz reaction tube was heated by a nichrome wound furnace, and its temperature was controlled to ±1°C. The pressure in the reaction zone was measured to ±0.05 mm Hg by a stainless steel transducer connected to the system by a Monel-to-glass ground joint. Ultradry argon of 99.995% purity as purchased was used as the purging gas.

Procedure

Before the system was put into use, it was passivated by repeated pressurization with fluorine, followed by prolonged evacuation. As a result of these steps, the concentration of impurities absorbed on the walls was reduced to a negligible value. For blank runs the pressure changed only 0.23 mm Hg in 7.5 hr, which for this study was insignificant.

High-purity copper (oxygen content less. than 0.002% as determined by vacuum fusion) was used for the metal specimens. The specimens in the form of 1.3 x 15.3 x 0.005 cm plates were cleaned by using (a) trichloroethane, (b) 20% nitric acid, and (c) distilled water, acetone, and alcohol rinses. All samples were given a standard preheat treatment consisting of heating 0.5 hr at 538°C in vacuum. After pretreatment, the furnace was adjusted to the appropriate temperature and fluorine was introduced to the desired pressure. The drop in pressure in the system of known volume was a measure of the fluo-
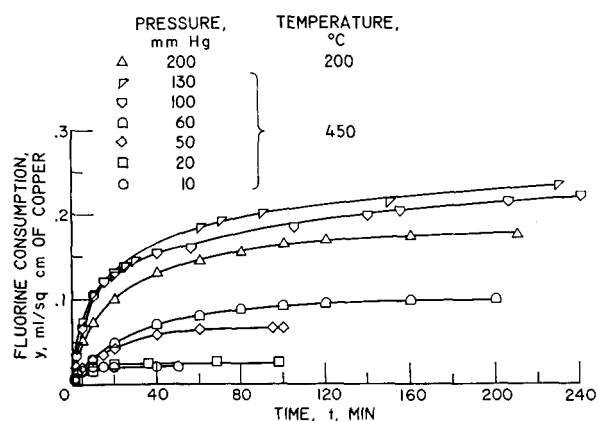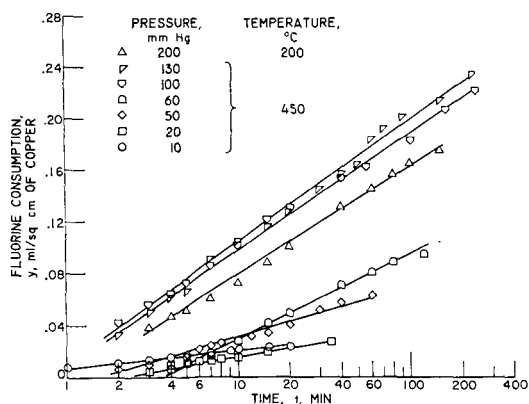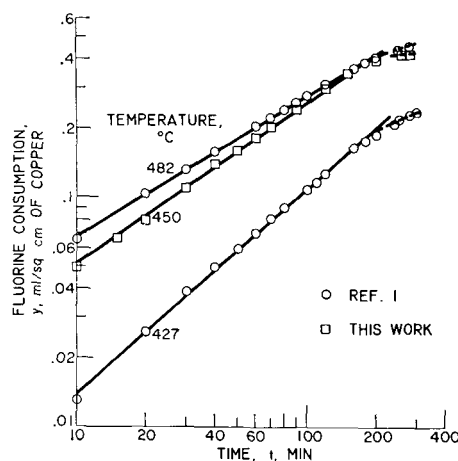
Fig. 2. Fluorination of copper

Fig. 3(b). Fluorination of copper, according to power law $y^n = kt$ at pressure of 200 mm Hg.

rine consumed. As fluorine was consumed, more fluorine was added to the reaction section to maintain the pressure within ±2 mm Hg of the initial value for the 50-130 mm runs and within ±1 mm Hg for the 10 and 20 mm runs. The run was continued until the consumption of fluorine had decreased to a negligible value. From the incremental pressure drops and the calibrated volume of the system, the amount of fluorine consumed was calculated. At the end of each run the furnace was cooled to 38°C before the fluorine was pumped out of the system through the soda lime traps. The system was then brought up to atmospheric pressure with argon and the copper plate was removed to a sample holder under flowing argon and sealed for later examination.

Results

The data obtained over a pressure range of 10-130 mm Hg at 450°C are shown in Fig. 2 where y, the fluorine consumed in milliliters per square centimeter of copper surface, is plotted as a function of t, the time in minutes. The two or more runs made at each pressure showed an average reproductibility in values of y of 6%. In Fig. 3(a) the data are plotted according to the logarithmic equation $y = K \log (at + c) + C$ where K is the logarithmic reaction rate constant, a is taken as unity with the dimension of reciprocal time, and c is taken as zero. These data are represented by this expression; however, at higher pressures the data no longer fit, and therefore the mechanism must be different. Data

taken at 200°C and 200 mm Hg appear to obey the same logarithmic law as the low pressure data at 450°C. The corrosion rate of the copper and fluorine as described by the aforementioned log law is therefore influenced by both temperature and pressure. In Fig. 3(b) data at 450°C and 200 mm Hg are plotted with similar data from ref. (1) according to the power law $y^n = kt$, and the consistency is quite good.

The variation of the rate constant, K, with pressure at 450°C is shown in the log plot of Fig. 4 where the rate constant is plotted as a function of the fluorine pressure according to the equation $\log K = m \log P-6.11439$. The slope, m, is the order of the reaction with respect to the fluorine pressure and has the value of 0.781.

An interesting event was observed in that the corroded metal specimens lost their passivity when subjected to heat and vacuum. In Fig. 5, at point B, the fluorine gas was pumped out of the reaction section to 0.1μ pressure and the pumping continued for 15 min. The reaction section was then pressurized with fresh fluorine to 10 mm Hg. As seen in Fig. 5, the reaction starts anew. The same logarithmic law also describes this second reaction; however, the logarithmic rate constant, K, is slightly lower for the second reaction. This same effect was observed by Brown *et al.* (3) if the pumping was continued for 4 days at 100°C; however, if the time of pumping

Fig. 3(a). Fluorination of copper, according to logarithmic law $y = K \log (at + c) + C$.
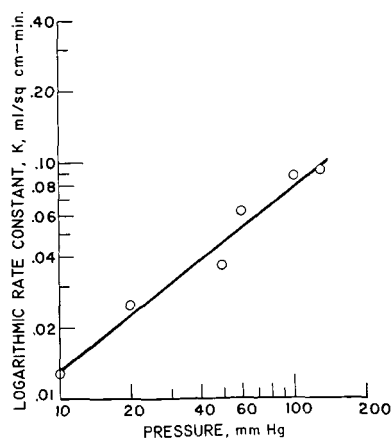
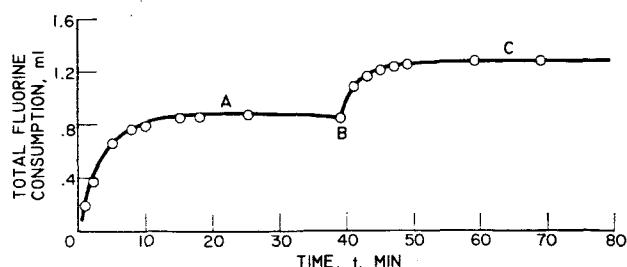Fig. 4. Effect of pressure on logarithmic rate constant K

Fig. 5. Interrupted fluorination of copper; A and C 450°C and 10 mm Hg pressure, B evacuated 15 min at 450°C.
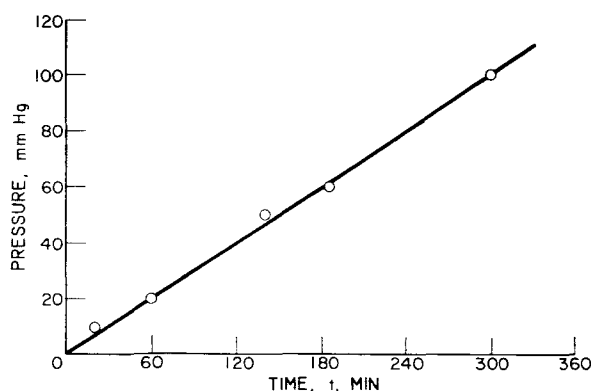

Fig. 6. Effect of pressure on passivation period of copper at 450°C

were shortened to 16 hr at the same temperature, they observed no effect. In our studies therefore, increasing the temperature by a factor of four decreased the pumping time by a factor of about 400.

The time it takes for the rate of reaction at 450°C to decrease to a negligible value ($<10^{-4}$ ml/cm²-min) is of interest. This time, which could be called the passivation period, is a linear function of pressure (shown in Fig. 6) where t, the time for the rate to decrease to the negligible value is plotted as a function of pressure. It must be pointed out that when the reaction reaches the negligible rate the logarithmic equation no longer holds.

Microscopic examination of the corrosion film showed the presence of both clear and red crystals. The red crystals are probably CuF and the colorless ones CuF_2. The total corrosion film was analyzed for copper and fluorine and the results indicate a F/Cu ratio of 1.11. Unfortunately because of the unstable nature of the corrosion products, they could not be positively identified. Most of the films formed at 450°C exfoliated on cooling, and examination of the metal surface underneath revealed many pits.

Discussion

In setting up a theoretical model to understand better the mechanism of the reaction between gaseous fluorine and a copper surface, it can be assumed that when the gas is introduced the reaction starts. The first thin film of reaction product forms a barrier between the two reacting phases, copper and fluorine. In order for the reaction to continue, therefore, it becomes necessary for either one or the other of the phases to migrate across this barrier. Based on evidence presented later, it can be postulated that the reaction includes at least the following three steps: (i) fluorine is absorbed on the outer surface;

(ii) fluorine migrates through the barrier layer; (iii) fluorine reacts with the copper. Initially, step (i) is predominant, but as soon as a film forms, step (ii) becomes rate controlling. The reaction in step (iii) is assumed to be very fast in comparison with the reactions in the other steps, and thus would not contribute significantly to the over-all reaction rate. If the migration through the barrier layer were strictly a diffusion controlled process, the data could be described by a parabolic rate law. As shown in Fig. 3(a), however, the data were best described by a logarithmic rate law, and therefore the reaction is not entirely diffusion controlled. Several theories based on various hypothetical rate-determining mechanisms have been put forward to explain the fact that under certain conditions the corrosion of metals obeys a logarithmic rate law (6). We have used the logarithmic rate equation as derived for the mechanism proposed by Vernon (7) who assumed that the reaction rate was dependent on the fraction of atoms penetrating the barrier layer. In addition we have assumed that this fraction is pressure dependent and therefore one would expect the rate constant K to vary with the pressure. This model is consistent with the data where K was found to vary with pressure according to the equation $\log K = m\log P - 6.11439$.

The logarithmic equation is

$$W = K \log (at + c) + C$$

where W is the weight of corrosion products formed and t is the time. c would be unity and C zero if the equation held from the onset where $t = 0$ and $W = 0$; however, in these experiments at $t = 0$, W has some finite value since a finite time is required for the reaction chamber to attain test pressure. Thus the equation does not hold at $t = 0$. C was calculated from the data in Fig. 3(a) assuming a and c to be equal to 1 and 0, respectively. The values of C and K are shown in Table I.

It is interesting to speculate on the location of the specific reaction. Two possibilities can be considered: (A) the copper can migrate through the barrier layer and react at the fluoride/fluorine interface or (B) the fluorine can migrate through the barrier layer and react at the fluoride/metal interface. Consider the following. The way in which the reaction rate constant varies with pressure infers at which interface the reaction is taking place. For example, reactions at the gas-corrosion layer interface usually are controlled by dissociation of the attacking diatomic gas and manifest themselves in a reaction rate constant that is a function of the square root of

Table I. Values of C and K

Temp, °C	Pressure, mm	K, ml/cm²-min	C, ml/cm³
450	10	0.013	0.008
450	20	0.025	—0.008
450	50	0.037	—0.005
450	60	0.063	—0.032
450	100	0.089	0.008
450	130	0.093	0.012
200	200	0.083	—0.004

the pressure (8). The experimental data show that this is not the relation between K and P under these test conditions. Second, it has been found in our earlier work (1) that pretreatment of the metal had a large effect on the rate. If the reaction were at the fluoride/fluorine interface, such a drastic effect on the rate would not be expected from the condition of the metal surface alone. Last, microscopic examination of the metal surface showed pits visible on the metal after the corrosion film was removed. Since pitting is not the result of an initial attack of a gas on a metal, but rather a localized attack for a period of time, pit formation could be favored by the gas having direct access to the metal. These points therefore tend to indicate that the reaction was carried out on the surface of the metal. From these data and from the work of Jarry (4) stating the probability of fluorine diffusion, fluorine is considered the migrating species in the copper fluorine reaction, and the reaction is considered to take place at the fluoride/metal interface.

Three possible ways for the fluorine to get to the metal would be (*a*) anion vacancy migration, (*b*) interstitial migration, and (*c*) grain boundary migration. Attack by migration along grain boundaries is common on metals at high temperature and has been shown to be the way fluorine reacts with nickel (2). This, of course, is possible also with copper; however, the mechanism by which fluorine migrates through the corrosion barrier is still in question.

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